



CT/AU98/00811

/509301 OCT 1998

CT

4

Patent Office
Canberra

PRIORITY DOCUMENT

SUBMITTED OR TRANSMITTED IN
COMPLIANCE WITH RULE 17.1(a) OR (b)

I, KIM MARSHALL, MANAGER EXAMINATION SUPPORT AND SALES,
hereby certify that the annexed is a true copy of the Provisional specification in
connection with Application No. PO 9462 for a patent by HOLBRAY PTY. LTD.
filed on 25 September 1997.

I further certify that the annexed specification is not, as yet, open to public inspection.



WITNESS my hand this Twelfth
day of October 1998

KIM MARSHALL
MANAGER EXAMINATION SUPPORT AND
SALES

Holbray Pty. Ltd.

A U S T R A L I A

Patents Act 1990

PROVISIONAL SPECIFICATION

for the invention entitled:

"Ion Exchange"

The invention is described in the following statement:

- 2 -

ION EXCHANGE

The present invention relates to ion exchange, in particular to ion exchange materials embedded in a polyurethane matrix. The present invention also relates to a process for the
5 recovery of metal cations and anions from solutions and slurries.

Ion exchange resins are generally manufactured in bead or particulate form from polymers such as polystyrene-divinyl benzene, acrylic, or phenol-formaldehyde condensates has been proposed that ion exchange fibres can be produced from either polyacrylonitrile onto which
10 active ligands can be attached, or polypropylene fibres on to which polystyrene-divinyl benzene can be grafted. Polyurethane foams have been proposed in PCT/AU93/00312 and PCT/AU94/00793 which are incorporated herein in their totality by reference.

Ligands can be attached to the surface of the particular ion exchange resins or fibres by
15 conducting one or more suitable chemical reactions.

To date, commercially manufactured resins have several disadvantages, including small particle size to provide a large surface-to-volume ratio, often lower selectivity for one metal ion species over other metal ion species prevalent in leach liquors and pK_a values which
20 prevent the resin loading anions at pH values above about 10. To provide additional ligand capacity, the resin beads are made macroporous. This is achieved by incorporating one or more porogens into the resin system during the polymerisation step. Such macroporosity, can lead to increased shattering of the beads in industrial processes.

25 The bulk density of the beads are not readily modified. Thus, the ions exchange beads being offered for application in for example, the gold industry have a tendency to float on the surface of the pulp during the cyanidation step. It is reported that this has led to loss of gold due to pilferage of the loaded beads.

30 In an effort to overcome this disadvantage, U.S. Patent 4,284,511 which is incorporated here

- 3 -

by reference, describes the addition of magnetic material, particularly finely divided particles of a non-corrosive, iron-chrome alloy to raise the bulk density of the polymer. This addition is proposed to be used with activated carbon, and polyurethane and similar materials when used in ion exchange columns, and in particular, in fluidised bed towers to enable higher fluid
5 flow rates to be achieved.

Other disadvantages of currently available ion exchange resins for metal ion recovery include:

- (a) purchase cost is high,
10
- (b) the present need for fine sized beads (in order to achieve a significant concentration of ligands) renders it difficult to recover them from pulps by screening,
- (c) stripping kinetics are slower and a more complex stripping regime is often required to
15 effectively recover the metal ion for electrowinning.

We have now found that by embedding an ion exchange material in a superabsorbent polyurethane foam superior ion exchange performance may be achieved. The present invention accordingly provides an ion exchange material comprising a superabsorbent
20 polyurethane foam having an ion exchange medium embedded therein.

The present invention also provides a process for the extraction of metal anions and cations from solutions and/or slurries including the steps of:

- 25 (a) contacting a metal ion-containing solution with an ion exchange material comprising a superabsorbent polyurethane foam having an ion exchange medium embedded therein;
- (b) separating the ion exchange material from the solution and/or slurry; and
- 30 (c) recovering the sorbed metal ions by elution from the resin.

These superabsorbent, hydrophilic polyurethane polymers are chemical entities which are well known to those skilled in the art. Methods for the preparation or application of these polymers are typically described in U.S. Patent Numbers

3,793,241; 3,854,535; 3,861,993; 3,890,254; 3,900,030; 3,903,232; 3,904,557; 4,110,508;
5 4,127,516; 4,137,200; 4,158,087; 4,160,076; 4,181,770; 4,266,043; 4,292,412; 4,314,034;
4,365,025; 4,337,645; 4,384,050; 4,384,051; 4,717,738; 4,725,628; 4,731,391; 4,740,528;
4,789,720; 4,798,876; 4,828,542; 5,065,752; 5,296,518; 5,591,779 and 5,624,971, which
are incorporated herein by reference.

10 The procedure for the manufacture of the prepolymers described in the above patents is either given within the description, or can be produced according to typical procedures as described in various publications relating to polyurethane chemistry, or as disclosed in U.S. Patent Nos. 2,726,219; 2,948,691; 2,993,013; 3,805,532 and 4,137,200.

15 In U.S. Patent 4,725,629 a superabsorbent polyurethane foam based upon an interconnecting polymer network of a crosslinked polyurethane and a cross-linked addition polymer containing a plurality of chain segments made up of functional groups containing repeating units which may be the same or different. These superabsorbent polymers are recommended for the manufacture of absorbent articles, especially disposable absorbent articles, such as
20 nappies, sanitary napkins, bedpads, incontinent pads, and the like.

Superabsorbent polyurethane foams preferably derived from an isocyanate-terminated poly(oxyalkylene) polyol having an isocyanate functionality greater than two and containing an addition polymer such as acrylamides, acrylate and methacrylate salts, etc. are disclosed
25 in U.S. Patent 4,731,391

British Patent 1,209,058 discloses a hydrophilic polyurethane foam in which a polyether polyol containing a block of ethylene oxide capped with propylene oxide to obtain hydrolytic stability is reacted with a polyisocyanate. Only small quantities of water are used. The foams
30 produced by this method have very poor water absorbing properties.

- 5 -

A superabsorbent polyurethane foam into which microcapsules of active ingredients are formed is described in U.S. Patent 4,828,542. The hydrophilic polyurethane prepolymer is foamed by mixing with water in the range of at least approximately 0.2/1 or greater and
5 preferably 1/1 or greater.

U.S. Patent 5,065,752 describes a superabsorbent, hydrophilic foam composition for wound dressings. The polyurethane foam is produced by the in-situ reaction product of an isocyanate-capped polyether prepolymer, a polymeric hydrophilic agent capable of absorbing water (such
10 as starch grafted copolymers of acrylate salts, or acrylamide salts), an adjuvant comprising a water-soluble alcohol, a wetting agent, and water.

U.S. Patent 5,591,779 discloses a process for preparing a superabsorbent polyurethane foam by reacting a suitable polyurethane prepolymer with water in the presence of a superabsorbent
15 polymer. The polyurethane prepolymer contains an oxyethylene content of at least 50% by weight. The amount of water required being 15 to 500 parts by weight of the weight of the prepolymer. At the start of the reaction, the temperature of the water being 10°C to 50°C higher than the temperature of the prepolymer.

20 The ion exchange medium may be any convenient ion exchange medium suitable for sorbing the desired metal ions from the solution and/or slurry. The ion exchange medium may be in the form of a bead, resin, fibre, foam, liquid or other convenient form.

Ion exchange mechanisms generally involve the exchange of ions in solution with the counter
25 ions associated with the ligands present in the extractant. The extractant may be either an insoluble solid inorganic or organic material, or a water-insoluble organic molecule. Thus, the desired extractant therefore contains anionic, cationic, or chelating ligands capable of recovering the desired metal ion from either solutions or from slurries.

30 Normally a metal ion exists in an aqueous solution as a hydrated ion with little or no tendency

- 6 -

to transfer to an organic phase. To enable an ion to transfer into an organic phase it is generally required that its charge must be neutralised and some, or all of its water of hydration has to be replaced by some other molecule or ion. For example, as reported by Irving and Damodaran the aurocyanide anion is generally weakly hydrated compared to other cyano-metallic complexes. Thus, its affinity for organic matrices relative to other more strongly hydrated anions, will be greater. A study on ionic mobilities in the Nernst layer has shown that the aurocyanide complex is significantly smaller and less hydrated than other cyano complexes. Examination of the hydration and ion pairing of the $\text{Au}(\text{CN})_2^-$ complex in aqueous solution does however require further investigation. Therefore, for a metal ion to be removed from the aqueous phase, these conditions can be met by:

- (a) complexing the ion with an ion of opposite charge to form a neutral species, which at the same time replaces some or all of the water of hydration around the metal ion,
 - (b) by formation of ion-association complexes which also provide for the formation of a neutral species with the extractant,
 - (c) by replacing the water of hydration with molecules of the solvent.
- An ion exchange medium, thus, may be a polymeric material in particulate, bead, fibre or foam form which carries a fixed positive or a fixed negative electrical charge. This electrical charge is balanced by ions of opposite sign, called counter ions. In solution, these counter ions are free to move within the resin matrix and therefore can be replaced, or exchanged, by other ions of the same sign. Thus systems employing chelating and acidic extractants are cation-exchange reactions, and those employing anion exchange systems are anion-exchange reactions.

Extractants containing C-O bonds are electron donating compounds, but alcohols being amphoteric, exhibit both donor and acceptor properties and resemble water in many ways. Thus, the formulation of superabsorbent polymers based upon poly(oxyethylene) glycol, and

- 7 -

if required sulphonic groups in the polymer structure, will enhance metal ion transport. Alcohols such as pentanol, tridecanol may be included into these superhydrophilic foams to improve solvation and also metal ion transport.

5

The preferred aromatic isocyanates are 2,4- and 2,6- toluene diisocyanates and methylene-bridged polyphenyl polyisocyanate mixtures which have a functionality of from about two to about four. These latter isocyanate compounds are generally produced by the phosgenation of corresponding methylene-bridged polyphenyl amines, which are conventionally produced
10 by the reaction of formaldehyde and primary aromatic amines, such as aniline, in the presence of hydrochloric acid and/or other acidic catalysts. Known processes for preparing polyamines and corresponding methylene-bridged polyphenyl polyisocyanates therefrom are described for example in U.S. Patent Nos. 2,683,730, 2,950,263, 3,012,008, 3,344,162 and 3,362,979.

15 Most preferred methylene-bridged polyphenyl polyisocyanate mixtures used herein contain about 20 to about 100 weight percent methylene diisocyanate isomers, with the remainder being polymethylene polyphenyl isocyanates having higher functionalities and higher molecular weights. Typical of these are polyphenyl polyisocyanate mixtures containing about 20 to 100 weight percent methylene diphenyldiisocyanate isomers, of which 20 to about 95
20 weight percent thereof is the 4,4' -isomer with the remainder being polymethylene polyphenyl polyisocyanates of higher weight and functionality of from about 2.1 about 3.5. These isocyanate mixtures can be prepared by the process described in U.S. Patent 3,332,979.

A commercially available MDI compound with especially desirable properties is Isonate 143L
25 which is produced by reacting MDI to form a carbodiimide and this material in turn then reacts to form a tri-functional cycloadduct. The mixture of MDI, the carbodiimide and the cycloadduct are in equilibrium. The mixture contains a major amount of pure diphenylmethane diisocyanate and minor amounts of carbodiimides and trifunctional cycloadducts of diphenylmethane diisocyanate. As described, the term derivatives of
30 diphenylmethane diisocyanate means products that have been made from MDI as a starting

- 8 -

material. It includes adducts dimers and trimers.

Other compounds which are useful are the isocyanate equivalents which produce the urethane linkages such as the nitrile carbonate, including the adiponitrile carbonate.

5

Also, both ethers and ketones allow a high degree of metal hydration in the solvent phase. For example, in the extraction of ferric chloride into ether, five molecules of water are associated with the extracted metal complex in the solvent phase and solvation numbers as high as 12 have been reported. Thus, superhydrophilicity enables these water molecules to be rapidly
10 transported through the polymer to the reactive sites.

The preferred components include a diol having greater than about 80% by weight of poly(oxyethylene) groups (such as PEG 1000) to provide the water-absorbing property, trimethylolpropane as the crosslinking agent, suspending or thickening agents and the
15 isocyanate used to cap or terminate the polyol is as described above.

The poly(oxyethylene) polyol may have a molecular weight of about 200 to about 20,000 and preferably between about 600 to about 6,000 and most preferably about 1000 to about 1400, with a hydroxyl functionality of about 2 or greater, but preferably from about 2 to 6 and most
20 preferably, 2.

The chain extenders which may be added to provide crosslinking strength to the foam are relatively short, low molecular weight monomeric polyols having three or four hydroxyl equivalents per mole. Such materials include glycerol, trimethylolpropane, trimethylolethane,
25 triethanolamine, pentaerithritol, or mixtures thereof.

Suspending or thickening agents include acrylic acid-based polymers such as Carbopol 934 and Carbopol 940. A neutralising agent such as sodium or ammonium hydroxide can be added.

30

- 9 -

The capping or termination reaction between the isocyanate and the polyol may be carried out in an inert moisture-free atmosphere such as under a nitrogen blanket, at atmospheric pressure at a temperature in the range of about 0°C to about 120°C for a period of time of up to about 24 hours depending upon the temperature and the degree of agitation and cooling or heating
5 applied to the reactor.

Superabsorbent microcellular resins and foams differ from the above polyurethane foams in that they are normally produced by the reaction of a suitably formulated isocyanate terminated polymer with a very significant excess of water. The polyol portion of the polymer is
10 generally based upon poly(oxyethylene) glycol, and the isocyanate component is generally TDI, MDI or MDI -based isocyanate or mixtures of both isocyanates.

Another very desirable property of the instant foams is the elimination of silicone surfactants from the formulation. It has been observed that these nonionic silicone-based raw materials
15 are specifically formulated so that they migrate to the surface of the rising foam to control the surface tension, promote nucleation and stabilise the rising foam by reducing stress concentrating in thinning cell-walls and counteract any defoaming effects caused by the presence of added, or generated/solid matter. Thus, these polymers remain at the surface of the cured polyurethane foam and interfere with subsequent interpenetration of a second
20 polymer or surface reactions conducted on the polyurethane foam cell walls.

The use of water soluble or water dispersable- surface active agents in urethane-urea foams is taught in U.S. Patent Nos. 3,890,254 and 4,160,076 to be critical to the attainment of many useful properties. Whereas, in U.S. patent 5,296,518 it was recognised that the choice
25 of certain isocyanate-capped high molecular weight molecules can be used in place of these surfactants. Being water soluble, and not taking part in the chemical reaction, they can be leached out of the foam. Thus, the presence of these surface active agents does not interfere with subsequent surface reaction such as interpenetration of a second polymer system.

30 Thermal reticulation whereby the windows or membranes are removed from individual cells

- 10 -

or bubbles which make up the foam structure. Reticulation results in a foam preferably having at least 95% of open cells and most preferably 99% open cells. Thermal reticulation of polyurethane foam is a known procedure to those skilled in the art and as disclosed for example is U.S. Patent Nos. 3,171,820 and 3,875,025 and 3,175,030. Reticulation is
5 achieved by providing a combustible mixture of an oxidiser material and an oxidisable material within the cells of the foam and then igniting the combustible mixture whereupon the cell windows or membranes are destroyed. It is also possible to swell the polyurethane foams in an organic solvent to increase the cell size.

10 Thus, as disclosed in U.S. Patent 4,985,467, the skeletal structure is completely open, and with such a structure, it will more rapidly absorb large amounts of liquid than an a non-reticulated cellular foam.

Poly(ethylene oxide) derivatives are good solvents for metal ions because of the Lewis-base
15 nature of the lone pairs on the oxygen atom. Macrocycles based on the ethylene oxide unit, the crown ethers, are amongst the strongest known complexing agents for cations. The reason for this is twofold, namely, the rings formed by ethylene oxide units tend to place oxygen atoms in favourable positions for the formation of coordination bonds with metal cations; and secondly, the excellent solvating properties of poly(ethylene oxide) .

20

To produce the desired superabsorbent ion exchange resins, several different methods may be adopted. In one preferred method, commercially produced solid ion exchange polymers may either be comminuted to reduce their particle size, or they may be used directly in the resin forming step, details of which appear below.

25

Alternatively, an another preferred method, organic liquid ion exchange materials may be imbibed into a solid sorbent in a suitable form such as particulates, sheets, fibres, foams. Such solid sorbents include styrene-divinyl benzene, acrylic, phenolformaldehyde, polyvinyl chloride, carbon, zeolites, vermiculite, etc and then incorporated into the superabsorbent
30 resin.

TBP addition to an uncharacterised polyurethane foam for the recovery and separation of nickel and palladium is described by Braun and Farag, Talanta (1972), 19,828-830. This foam would not have provided sufficient hydrophilicity as enunciated in the present disclosure.

5

A number of phosphates, including di(2-ethylhexyl) phosphate, and particularly tri-n-butyl phosphate (TBP) have been extensively employed in solvent extraction systems for metal ions. TBP has been included in a number of patents relating to gold recovery from chloride and cyanide solutions. It is used in industrial process to remove arsenic from copper solutions. It

10 is proposed as a suitable extractant for zinc from acid solution.

As a general rule, the extractive power of phosphorous containing extractants increases with an increase in the number of carbon-phosphorous bonds over the series, phosphate-phosphonate-phosphine oxide. The solubility of neutral organophosphorus compounds in
 15 water decreases in the order phosphine oxides > phosphinates > phosphonates > phosphates. This is as a result of the increasingly polar nature of the phosphonyl group. It should be noted that in acid solutions these extractants have low solubility, but as the pH increases, so solubility increases. It is known that the phosphoryl oxygen forms hydrogen bonds with water, and the bond energy is approximately 5kcal/mole. The more basic oxygen
 20 in a phosphonate gives a hydrogen bond energy of about 7-8 kcal/mole.

Dialkyl phosphorodithioic acids, phosphonates, dialkylthiophosphate, sulphur-containing methyl phosphonates and ketophosphonates and the trialkyl thiophosphates have been shown to be highly selective for gold, silver and mercury. Triiso-octyl thiophosphate and tri-n-butyl
 25 thiophosphate are similar to their trialkyl phosphate counterparts except that the P=O has been replaced by a P=S group. The semipolar sulphur atom is the sole structural difference between the two types. Handley and Dean proposed that the trialkyl thiophosphates probably act by solvating an electrically neutral ion association complex.



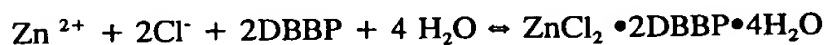
The ion association bonding occurs through the P=S group. The semipolar sulphur atom has very little electron donating ability, and will bond only to ions of high field strength. Silver and mercury fit this criteria and also are amongst those metals which prefer sulphur-containing ligands. These extractants have been shown to reduce Au (III) to Au°.

5

Extraction of cadmium, zinc, and mercury have been demonstrated to be possible with thiophosphorus compounds containing a P-SH group. The affinity of these metals for sulphur increases in the order zinc < cadmium < mercury. The extractants studied included di-n-butyl thiophosphite (DBTP) and the di-n-butyl ester of 2-hydroxypropan-2-thiophosphonic
10 acid (DBPrPS). It has been reported that mercury and gold (III) chloride are extracted from hydrochloric acid solutions with triisobutylphosphine sulphide (Cyanex 471X). This extractant is particularly selective for silver and for the separation of palladium and platinum.

In extraction of metal ions from acidic media generally two molecules of TBP are involved
15 in the extracted species. Furthermore, as the acid concentration increases so extraction of metal increases until a maximum is reached above which extraction decreases.

In a similar manner, dibutyl butyl phosphonate (DBBP) has been employed for the extraction of gold, and PGM's, and for zinc. DBBP has a high selectivity and loading capacity for zinc
20 in chloride solutions resulting from ferric chloride leaching of a complex sulphide ore. Extraction was found to be independent of pH. He reported that two moles of DBBP react with one mole of zinc. As a solvating extractant, extraction occurs as the extractant molecules replace water molecules in the primary hydration sheath of the extracted species. From the determination of free activities of water and free chloride ions it was shown that four water
25 molecules and two chloride ions are involved for each extracted zinc species. The extraction reaction may be written as follows:



30 DBBP may form dimers at concentrations higher than $3.7 \times 10^{-1} \text{ mol/dm}^3$ and thus at lower

- 13 -

concentrations the plot of Log [DBBP] versus Log E a straight line with a slope of two is obtained. At concentrations higher than $3.7 \times 10^{-1} \text{ mol/dm}^3$ the slope is greater than two possibly because the extraction equilibrium changes in favour of extraction when DBBP dimers form. DBBP may form dimers at higher free DBBP concentrations in a manner similar
5 to that reported by Burger for tributyl phosphate.

Industrial applications of ion exchange resins are many, particularly in the treatment of boiler feedwater. U.S. Patent 4,069,119 which is incorporated here by reference, describes the application of ion exchange resins to recover copper from dilute solutions emanating from vat
10 leaching of copper ores. This patent describes the beneficial effect of recovery from solutions containing significant levels of dissolved silica. This patent describes ion exchange resins in bead form, including polyurethane foams and porous beads impregnated with conventional organic solvent extraction agents to produce materials which may be employed as ion exchange beads in this application.

15

EXAMPLES

Example 1.

20 Into a suitable mixing container was added:

	Separan Solution (1 % in water)	25g
	Water	75g
	Pluronic L62	1.0g
25	Vitrocele V912 (ion exchange beads)	20g
	Ferrosilicon powder	20g
	Dyestuff	1 drop

The ingredients were thoroughly mixed together and then poured into a second container
30 containing 50 grams of the following mixture:

- 14 -

Prepolymer	10g
Isonate 143L	30g

TOTAL 10g + 30g = 40g

Example 2

- 5 In the examples in which a liquid organic extract was used, the following procedure was adopted:

	Styrene-divinyl benzene resin (XAD-16 milled)	10g
	LIX 84I	10g
10	Polyethylene glycol 1000	2g

The solid resin and the organic extractant were combined together and heated to about 35°C with constant stirring. Once the extractant was fully imbibed into the resin, the PEG1000 was added and stirring continued. A dry powder was obtained.

15

This powder was then mixed with the following:

	Powder	15g
	Ferrochrome	10g
	Water	20g
20	1% Separan Solution	5g
	Pluronic L62	0.75g

To this mixture was added:

	Prepolymer	20g
25	Isonate 143L	5g

DATED this 25th day of September 1997

Holbray Pty Ltd

By DAVIES COLLISON CAVE

30 Patent Attorneys for the applicant

THIS PAGE BLANK (USPTO)